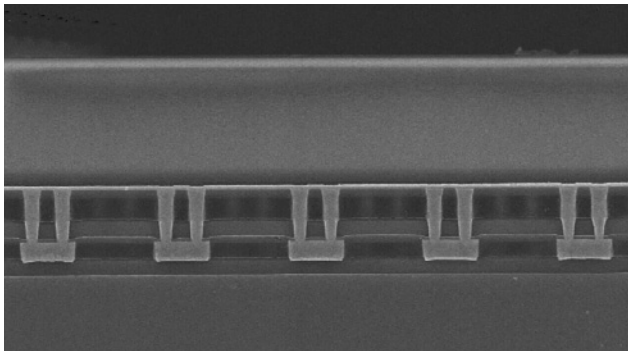
ELECTRONIC MATERIALS
MICROELECTRONIC TECHNOLOGIES

# ULTRAFILL™ 3003 ACID COPPER ELECTROPLATING SOLUTION

For Advanced Interconnect Applications

## DESCRIPTION

Ultrafill 3003 is a proprietary acid copper electrochemistry uniquely formulated for dual damascene applications in high volume manufacturing. This chemistry has been designed for the 65 and 45 nm technology nodes but can be easily back integrated for less aggressive technology nodes. The Ultrafill 3003 system consists of associated products manufactured to strict industry specifications. The highly purified copper electrolyte ensures reproducible results with respect to film deposit characteristics and functional properties.



90 nm Dual Damascene Structure

## FEATURES AND BENEFITS

- Consistent, reproducible, void free filling of features through the 45 nm technology node
- Ideally suited for dual damascene applications
- Capable of controlled Cu film impurities to exceed via stress-migration (VSM) and electro-migration (EM) reliability testing
- Fully characterized organic additive system specifically engineered for bottom-up feature-filling at a variety of acid concentrations
- Delivers a smooth, highly reflective copper surface for ease of post plating inspection
- Provides excellent globally uniform deposit for over a variety of feature sizes and pattern densities reducing the challenges of subsequent CMP processing
- Ultrafill 3003 products are manufactured consistently to tight tolerances to maximize precision of bath control maximizing process latitude
- Consistent results throughout the lifetime of the bath

## ULTRAFILL 3003 SYSTEM

### Components

- Ultrafill EC-3003 Electrolyte
- Ultrafill A-3003 Accelerator
- Ultrafill S-3003 Suppressor
- Ultrafill L-3003 Leveler

### Analytical Standards

- Ultrafill 3003 VMS
- Ultrafill CVS rA-3003 Standard
- Ultrafill CVS rS-3003 Standard
- Ultrafill CVS rL-3003 Standard

## FILM PROPERTIES

| | |
|---|---|
| Resistivity: | <1.8 μ-Ω-cm, post-anneal |
| Stress: | <50 Mpa, post-anneal |
| Via Fill: | 65 nm >5:1 AR |
| Trench Fill: | 50 nm >10:1 AR |
| Surface Smoothness: | <8 nm (@ 1 μm) across a blanket wafer |
| Reflectivity (@ 480 nm vs. polished Si): | >135% @ 1 μm |
| Leveling (overplating): | <1,000Å over dense arrays |
| Pass: | All electrical and reliability tests |



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## INORGANIC COMPONENT CONCENTRATIONS

Ultrafill EC-3003 Electrolyte comprises 98% of the bath volume and is the source of copper, chloride and sulfuric acid for the electrolytic deposition process. After a fresh bath is made, the concentration of each inorganic component should be measured to verify the bath make up. The concentration of each inorganic component should be monitored on a daily basis when the tool/bath is in operation. Under typical operation, replenishment of the inorganic components is not required. There are a variety of methods, which can be used for the analysis of the inorganic components. These methods are available through your plating tool supplier or upon request from your local Rohm and Haas Electronic Materials Microelectronic Technologies Representative.

## ORGANIC COMPONENT CONCENTRATIONS

Ultrafill A-3003 Accelerator, Ultrafill S-3003 Suppressor & Ultrafill L-3003 Leveler provide the source of organic 'additive' components for the bath. The organic bath components are consumed through solution drag out, solution pumping and the electrodeposition process. The organic bath components should be added to the bath as needed to maintain the recommended concentrations. Organic additive component replenishment rates are dependent on operating conditions, tool design, sump volume and solution agitation. Component replenishment will require adjustment based upon tool specifications and individual process methods. The concentrations of the organic additive components can be measured by standard cyclic voltameteric stripping methods (CVS). These methods are available through your metrology tool supplier or upon request from your local Rohm and Haas Electronic Materials Microelectronic Technologies Representative.

## ANALYTICAL STANDARDS

Bath metrology is accomplished utilizing standard CVS methods. In order to maintain optimal performance the use of Rohm and Haas Electronic Materials Microelectronic Technologies analytical standards ensures accurate and reproducible results. Ultrafill CVS rA-3003 Standard, Ultrafill CVS rS-3003 Standard & Ultrafill CVS rL-3003 Standard provide the reference source for metrology purposes only. The analytical standards should be added to the metrology unit on an as needed basis to maintain the appropriate volumes for operation. These methods are available through your metrology tool supplier or upon request from your local Rohm and Haas Electronic Materials Microelectronic Technologies Representative.

## OPERATING CONDITIONS

### Bath Parameters

Each bath parameter needs to be monitored and controlled to ensure optimum plating performance. Table 1 lists the bath parameters and operating ranges that have demonstrated robust overall performance for the Ultrafill 3003 system. Bath parameter target values are recommended for plating system start up. Optimum plating conditions will vary depending on seed layer and feature size.

**Table 1. Critical Ultrafill 3003 Bath Parameters**

| Parameter | Recommended | Range |
|---|---|---|
| Ultrafill EC-3003 Electrolyte Solution | 972 ml/l | — |
| Copper Metal | 40.0 g/l | 37.5–42.5 g/l |
| Sulfuric Acid | 10 g/l | 5–15 g/l |
| Chloride Ion | 50 ppm | 45–55 ppm |
| Ultrafill S-3003 Suppressor Solution | 5 ml/l | 3–7 ml/l |
| Ultrafill A-3003 Accelerator Solution | 12 ml/l | 10–14 ml/l |
| Ultrafill L-3003 Leveler Solution | 2.5 ml/l | 2–3 ml/l |
| Temperature | 23°C | 20–25°C |
| Current Density | 25 mA/cm$^2$ | 5 - 60 mA/cm$^2$ |

### Bath Maintenance

1. Maintain solution volume with DI water
2. Maintain bath constituents at recommended concentrations

### Bath Make-up

**Note:** Please read the Ultrafill 3003 Material Safety Data Sheets (MSDS) and use adequate ventilation before handling any product.

1. Clean the equipment per the tool manufacturer's recommended procedure or see below for general cleaning instructions.
2. Fill system reservoir tank with the required amount of Ultrafill EC-3003 Electrolyte solution.

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3. To film the copper anode (phosphorous content 0.02–0.06%) use a 90 minute burn-in at 10–15 mA/cm$^2$ with the electrolyte solution only. Alternatively follow the recommended procedure provided by the tool manufacturer. Anode conditioning for a new bath is critical for optimizing plating performance as well as stabilization of bath additives.
4. Add the required amount of Ultrafill S-3003 Suppressor solution.
5. Add the required amount of Ultrafill A-3003 Accelerator solution.
6. Add the required amount of Ultrafill L-3003 Leveler solution.
7. Allow the dosed bath to re-circulate throughout the plating tool for 30 minutes.
8. Bring the plating bath up to operating temperature (23°C ±3°C)

### Bath Volume

### Metrology and Replenishment

The bath volume will decrease over time due to evaporation of water and solution drag out on the wafer surface. Losses should be compensated by DI water additions and adjustment of bath additives to recommended levels. Rohm and Haas Electronic Materials Microelectronic Technologies strongly recommends using an on-line electrochemical analysis system. These systems supply the hardware and software for electrochemical analysis of the bath composition. These bath analysis systems can also make compensating adjustments to the bath by using the plating tool auto replenishment system. Several system suppliers have developed methods of electrochemical analysis for the Ultrafill 3003 copper plating chemistry. In the event that an excessive amount of a specific component has been added to the plating bath, it is recommended that the bath be drained to the correct volume for the overdosed component. The bath should then be brought to the volume by dosing all bath components.

## BATH LIFE/YIELD

A properly controlled and replenished bath will yield approximately 1,600–2,000 wafers (200 mm) per liter of bath volume with a deposit thickness of approximately 1 µm. Bath life is dependent on throughput as well as frequency of use. Systems can be operated in either batch or bleed and feed mode for extended bath life.

## EQUIPMENT CLEANING

1. Fill the empty tank with clean DI water and circulate.
2. Discharge the rinse water and remove any precipitates.
3. Fill the tank with 10–20 g/l of potassium hydroxide or sodium hydroxide solution and circulate for at least 60 minutes.
4. Rinse the tank and all lines thoroughly with DI water.
5. Fill the tank with 10–20 g/l sulfuric acid and circulate for at least 60 minutes.
6. Thoroughly rinse the tank and all lines again with DI water.
7. Fill tank with Ultrafill EC-3003 Electrolyte solution and begin bath preparation procedures.

## HANDLING PRECAUTIONS

Before using this product, consult the Material Safety Data Sheet (MSDS)/Safety Data Sheet (SDS) for details on product hazards, recommended handling precautions and product storage.

**CAUTION!** Keep combustible and/or flammable products and their vapors away from heat, sparks, flames and other sources of ignition including static discharge. Processing or operating at temperatures near or above product flashpoint may pose a fire hazard. Use appropriate grounding and bonding techniques to manage static discharge hazards.

**CAUTION!** Failure to maintain proper volume level when using immersion heaters can expose tank and solution to excessive heat resulting in a possible combustion hazard, particularly when plastic tanks are used.

## STORAGE

Store products in tightly closed original containers at temperatures recommended on the product label.

## DISPOSAL CONSIDERATIONS

Dispose in accordance with all local, state (provincial) and federal regulations. Empty containers may contain hazardous residues. This material and its container must be disposed in a safe and legal manner.

It is the user's responsibility to verify that treatment and disposal procedures comply with local, state (provincial) and federal regulations. Contact your Rohm and Haas Electronic Materials Technical Representative for more information.

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